

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicant: Premakaran T. Boaz and John Pereira

Application No.: 10/802,387 Group: 1742

Filed: March 17, 2004 Examiner: Not assigned

Confirmation No.: 3670

For: Solder Composition

CERTIFICATE OF MAILING	
I hereby certify that this correspondence is being deposited with the United States Postal Service with sufficient postage as First Class Mail in an envelope addressed to Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450	
on <u>07/22/04</u>	<u>Ellen T. Spear</u>
Date	Signature
<u>Ellen T. Spear</u>	
Typed or printed name of person signing certificate	

PETITION UNDER 37 C.F.R. § 1.47(a) AND TRANSMITTAL OF DECLARATION

Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

Sir:

Antaya Technologies and John Pereira hereby Petition that the above captioned application be accepted under 37 C.F.R. § 1.47(a). The Petition fee required under 37 C.F.R. § 1.17(h) is provided herewith.

One of the inventors, Premakaran T. Boaz (Prem Boaz), has not returned a signed Declaration for the above-referenced application despite attempts.

07/27/2004 DTESSEM1 00000069 10802387

05 FC:1460

130.00 OP

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On March 17, 2004, the application materials for the above-referenced application, including the specification, claims, abstract and informal drawings ("the application papers") were deposited with the U.S. postal service under 37 C.F.R. § 1.10.

On April 12, 2004, John Pereira of Antaya Technologies forwarded a package including a copy of all the application papers and Declaration and Assignment forms to Prem Boaz by Certified Mail to his last known address. Copies of this package, cover letter and certified mail receipt are attached as Exhibit A. On April 28, 2004, Mr. Pereira sent an email message to Prem Boaz asking him to sign the Declaration and Assignment. A copy of the email is attached as Exhibit B. On May 26, I also forwarded by certified mail, a copy of the package previously forwarded to Mr. Boaz to his attorney Daniel Bliss, copy attached with certified mail receipts as Exhibit C.

Mr. Boaz as of this date has still not returned the executed documents despite attempts to obtain his signature.

The last known address of Premakaran T. Boaz is as follows:

16842 Yorkshire Street
Livonia, Michigan 48154

The executed Declaration for the other inventor, John Pereira, is being submitted herewith in response to the Notice to File Missing Parts dated June 4, 2004. A copy of the Notice is enclosed.

The attached check in the amount of \$1,476.00 includes payment of the filing fees, surcharge and fee required under 37 C.F.R. § 1.17(h).

Please charge any additional fees due in this matter to Applicant's Attorney Deposit Account No. 08-0380. A copy of this letter is enclosed for accounting purposes.

Respectfully submitted,

HAMILTON, BROOK, SMITH & REYNOLDS, P.C.

By 

Darrell L. Wong

Registration No. 36,725

Telephone: (978) 341-0036

Facsimile: (978) 341-0136

Concord, MA 01742-9133

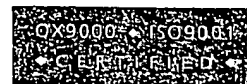
Date: 



RECEIVED

MAY 20 2004

HAMILTON, BROOK,
SMITH & REYNOLDS, P.C.
April 12, 2004



Via Certified Mail

Mr. Prem Boaz
16842 Yorkshire Street
Livonia, Michigan 48154

COPY

Re: Solder Composition Patent Application

Dear Prem:

It has taken Antaya some time to move and rebuild our solder manufacturing equipment but we are now ready to produce product. Under Antaya's ongoing agreement with you, Antaya is authorized to apply for patents resulting from the development activities with you for the solder composition. Please find enclosed a copy of a patent application that we have recently filed for solder compositions resulting from the developmental activities in which you and I are co-inventors. Additionally enclosed is a Declaration for Patent Application which, after you read the application, is for your signature as an inventor. Please sign it in blue ink. Any corrections to your name, address and citizenship should be initialed and dated in the margin. An Assignment document is also enclosed and should be signed in blue ink in the presence of a Notary Public.

Finally, since we paid for the filing of your previous application, we would like to assume responsibility for that case.

If you have any questions, please call myself or Stephen to discuss.

Very truly yours,

A handwritten signature in dark ink, appearing to read "John Pereira", with a stylized, flowing script.

John Pereira

Enclosures

@PFDdesktop::ODMA/MHODMA/HBSR05;iManage;454380;1

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Sent To

Premakaran Boaz

Street, Apt. No.,
or PO Box No.

16842 Yorkshire Street

City, State, ZIP+4

Livonia, MI, 48154

PS Form 3800, January 2001

See Reverse for Instructions

2001 1140 0001 0741 9101

John Pereira

From: John Pereira
Sent: Wednesday, April 28, 2004 11:31 AM
To: Prem T Boaz (E-mail)
Subject: FW: Patent Application for Solder Composition

Dear Prem:

In regard to the patent application entitled "Solder Composition" and the accompanying Declaration for Patent Application which we mailed to you via USPS Certified Mail on April 22nd, can you please sign the Declaration and the Assignment.

Regards,
John

HAMILTON
BROOK
SMITH &
REYNOLDS, P.C.

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530 VIRGINIA ROAD
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CONCORD, MA 01742-9133
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FAX (978) 341-0136
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May 26, 2004

MUNROE H. HAMILTON
(1906-1984)

DAVID E. BROOK
JAMES M. SMITH
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DARRELL L. WONG

OF COUNSEL
ELIZABETH W. MATA

PATENT AGENTS
SUSAN M. ABELLEIRA
ALEXANDER AKHIEZER
KRAIG ANDERSON
JESSE A. FECKER
LUCY LUBASHEV
PAMELA A. TORPEY
KAREN J. TOWNSEND
ROBERT H. UNDERWOOD

TECHNOLOGY SPECIALISTS
KAMILAH ALEXANDER
PAUL G. ALLOWAY
SUSAN C. KELLY
BOOYONG SHIM LIM
VIVIAN J. TANNOKH-MAGIN
MICHAEL M. YAMAUCHI

MICHAEL KEWESHAN
ADMINISTRATIVE DIRECTOR

BARBARA J. FORGUE
ADMINISTRATOR OF
PATENT AND
TRADEMARK PRACTICE

Certified Mail

Daniel H. Bliss, Esq.
Bliss McGlynn, P.C.
2075 West Big Beaver Road, Suite 600
Troy, Michigan 48084

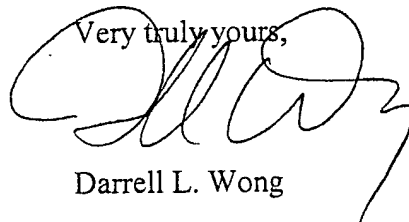
Re: Solder Composition Patent Application

Dear Mr. Bliss:

We represent Antaya Technologies Corporation of Cranston, Rhode Island in certain legal matters. Antaya has filed a patent application in the U.S. Patent Office entitled "Solder Composition", in which Premakaran Boaz is a co-inventor. Antaya forwarded to Mr. Boaz on April 12, 2004, via certified mail, the enclosed package containing a cover letter, a copy of the patent application, and attached Declaration and Assignment documents for Mr. Boaz's signature. However, Antaya has not received any word from Mr. Boaz.

We understand that you have been representing Mr. Boaz in patent matters, so we trust that you will make sure that he receives the enclosed package just in case he did not receive Antaya's previous mailing.

Very truly yours,



Darrell L. Wong

DLW/ets
Enclosures

cc: Mr. John Pereira

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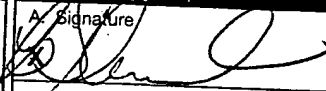
Daniel H. Bliss, Esq.
Bliss McGlynn, P.C.
2075 W. Big Beaver Rd.
Suite 600
Troy, MI 48084

2. Article Number

(Transfer from service label)

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A. Signature

☐ Agent☐ Addressee

B. Received by (Printed Name)

C. Date of Delivery

6-1-2004

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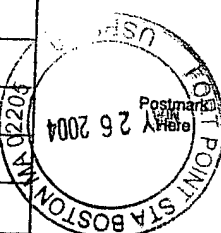
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Sent To

Daniel H. Bliss, Esq., Bliss McGlynn, P.C.

Street, Apt. No.,

or PO Box No.

2075 W. Big Beaver Rd., Ste. 600

City, State, ZIP+4

Troy, Michigan 48084

PS Form 3800, April 2002

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ANTAYA
TECHNOLOGIES
CORPORATION

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MAY 20 2004

HAMILTON, BROOK,
SMITH & REYNOLDS, P.C.
April 12, 2004



Via Certified Mail

Mr. Prem Boaz
16842 Yorkshire Street
Livonia, Michigan 48154

COPY

Re: Solder Composition Patent Application

Dear Prem:

It has taken Antaya some time to move and rebuild our solder manufacturing equipment but we are now ready to produce product. Under Antaya's ongoing agreement with you, Antaya is authorized to apply for patents resulting from the development activities with you for the solder composition. Please find enclosed a copy of a patent application that we have recently filed for solder compositions resulting from the developmental activities in which you and I are co-inventors. Additionally enclosed is a Declaration for Patent Application which, after you read the application, is for your signature as an inventor. Please sign it in blue ink. Any corrections to your name, address and citizenship should be initialed and dated in the margin. An Assignment document is also enclosed and should be signed in blue ink in the presence of a Notary Public.

Finally, since we paid for the filing of your previous application, we would like to assume responsibility for that case.

If you have any questions, please call myself or Stephen to discuss.

Very truly yours,

John Pereira

Enclosures

@PFDesktop\ODMA\MHODMA\HBSR05\iManage\454380;1

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Declaration for Patent Application

[] Supplemental (37 C.F.R. §1.67)

As a named inventor, I hereby declare that:

My residence, mailing address and citizenship are as stated next to my name;

I believe I am the original, first and sole inventor (if only one name is listed) or an original, first and joint inventor (if plural names are listed in the signatory page(s) commencing at page 2 hereof) of the subject matter which is claimed and for which a patent is sought on the invention entitled

SOLDER COMPOSITION

the specification of which (check one)

[] is attached hereto.

[X] was filed on March 17, 2004 as United States Application Number 10/802,387.

[] was filed on [PCT Filing Date] as PCT International Application No. [PCT Appl'n No.] [and assigned United States Application No. []].

[] and was amended on [] (if applicable).

I hereby state that I have reviewed and understand the contents of the above-identified specification, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose information which is material to patentability as defined in 37 C.F.R. §1.56, including for continuation-in-part applications, material information which became available between the filing date of the prior application and the national or PCT international filing date of the continuation-in-part application.

I hereby claim foreign priority benefits under 35 U.S.C. 119 or 365 of any foreign application(s) for patent or inventor's certificate, or of any PCT international application which designated at least one country other than the United States of America, listed below and have also identified below, by checking the box, any foreign application for patent or inventor's certificate, or of any PCT international application having a filing date before that of the application on which priority is claimed:

<u>Prior Foreign Application(s)</u>			Priority Not Claimed	Certified Copy Filed?	
				YES	NO
<u>(Number)</u>	<u>(Country)</u>	<u>(Day/Month/Year filed)</u>	[]	[]	[]
<u>(Number)</u>	<u>(Country)</u>	<u>(Day/Month/Year filed)</u>	[]	[]	[]
<u>(Number)</u>	<u>(Country)</u>	<u>(Day/Month/Year filed)</u>	[]	[]	[]

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

Full name of sole

or first inventor Premakaran T. Boaz

Inventor's Signature _____ Date _____

Residence 16842 Yorkshire Street, Livonia, Michigan, 48154

Citizenship USA

Mailing Address same

Full name of second joint

inventor, if any John Pereira

Inventor's Signature _____ Date _____

Residence 223 Agricultural Avenue, Rehoboth, Massachusetts, 02769

Citizenship USA

Mailing Address same

Full name of third joint

inventor, if any _____

Inventor's Signature _____ Date _____

Residence _____

Citizenship _____

Mailing Address _____

Full name of fourth joint

inventor, if any _____

Inventor's Signature _____ Date _____

Residence _____

Citizenship _____

Mailing Address _____

Joint

ASSIGNMENT

WHEREAS, we, **Premakaran T. Boaz and John Pereira**, have invented a certain improvement in **Solder Composition** described in an application for Patent,

- ☐ the specification of which is being executed on even date herewith and is about to be filed in the United States Patent Office (*use for utility (37 CFR § 1.53(b)) and design filings only*);
- ☐ is about to be filed in the United States Patent Office as a Provisional Application;
- ☒ the specification of which is United States Application No. **10/802,387**, filed **March 17, 2004**;
- ☐ the specification of which is a Patent Cooperation Treaty Application, International Application No. [], which designates the United States of America;
- ☐ which was patented under United States Patent No. [].

WHEREAS, **Antaya Technologies Corporation** (hereinafter "ASSIGNEE"), a corporation organized and existing under the laws of the **State of Rhode Island**, and having a usual place of business at **72 Fenner Street, Cranston, Rhode Island, 02910**, desires to acquire an interest therein in accordance with agreements duly entered into with us;

NOW, THEREFORE, to all whom it may concern be it known that for and in consideration of said agreements and of other good and valuable consideration, the receipt of which is hereby acknowledged, we have sold, assigned and transferred and by these presents do hereby sell, assign and transfer unto said ASSIGNEE, its successors, assigns and legal representatives, the entire right, title and interest in and throughout the United States of America, its territories and all foreign countries, in and to said invention as described in said application, together with the entire right, title and interest in and to said application and such Letters Patent as may issue on said invention; said invention, application and Letters Patent to be held and enjoyed by said ASSIGNEE for its own use and behalf and for its successors, assigns and legal representatives, to the full end of the term for which said Letters Patent may be granted as fully and entirely as the same would have been held by us had this assignment and sale not been made; we hereby convey all rights arising under or pursuant to any and all international agreements, treaties or laws relating to the protection of industrial property by filing any such applications for Letters Patent. We hereby acknowledge that this assignment, being of the entire right, title and interest in and to said invention, carries with it the right in ASSIGNEE to apply for and obtain from competent authorities in all countries of the world any and all Letters Patent by attorneys and agents of ASSIGNEE's selection and the right to procure the grant of all such Letters Patent to ASSIGNEE for its own name as assignee of the entire right, title and interest therein;

AND, we hereby further agree for ourselves and our executors and administrators to execute upon request any other lawful documents and likewise to perform any other lawful acts which may be deemed necessary to secure fully the aforesaid invention to said ASSIGNEE, its

successors, assigns and legal representatives, but at its or their expense and charges, including the execution of applications for patents in foreign countries, and the execution of any future applications including substitution, reissue, divisional or continuation applications, and preliminary or other statements and the giving of testimony in any interference or other proceeding in which said invention or any application or patent directed thereto may be involved;

AND, we do hereby authorize and request each Patent Office and the Commissioner of Patents of the United States to issue such Letters Patent as shall be granted upon said invention to said ASSIGNEE, its successors, assigns, and legal representatives.

IN TESTIMONY WHEREOF, we have hereunto set our hands and affixed our seals the date set forth below.

Inventor's Signature: _____

Premakaran T. Boaz

State/Commonwealth _____

of _____

County of _____

Then personally appeared before me the above-named **Premakaran T. Boaz** and acknowledged that he/she executed the foregoing instrument as his/her free act and deed this _____ day of _____, 20____.

(SEAL)

Notary Public

(print name)

My Commission expires ____/____/____

Inventor's Signature: _____

John Pereira

State/Commonwealth _____

of _____

County of _____

Then personally appeared before me the above-named **John Pereira** and acknowledged that he/she executed the foregoing instrument as his/her free act and deed this _____ day of _____, 20____.

(SEAL)

Notary Public

(print name)

My Commission expires ____/____/____

-1-

Date: 03/17/04

Express Mail Label No.

EV214952948US

Inventors: Premakaran T. Boaz and John Pereira

Attorney's Docket No.: 2678.2011-000

SOLDER COMPOSITION

BACKGROUND

Generally speaking, solder is a material used to provide connections either between various items or to secure an item to a substrate. Solder is used in several technical fields, such as electrical, mechanical, or thermal; however, the specific composition of solder or type of solder alloy varies widely between technical fields and even within a given field, depending on the application. Traditionally, solder largely consisted of lead as a result of its physical and chemical characteristics (i.e., wettability, melting point, rate of thermal expansion, etc.); however, lead solder became known as a source of environmental pollution and federal legislation mandated a reduction in the content of lead in solder.

As a result, lead-free solder was introduced into various technical fields and is currently used for numerous applications without issue. As disclosed in U.S. patent numbers 5,066,544; 5,918,795; and 6,371,361, lead-free solder or reduced lead content solder is successfully applied to soldering electronic components in both the microelectronic and conventional electronic fields.

However, there exist other technical fields where the aforementioned lead free solders are deficient. Within the technical field of soldering onto a substrate, such as an automobile window or windshield, known lead-free solders are less desirable because they contain alloy compositions which possess a coefficient of thermal expansion nearly twice that of a glass substrate. As a result, the solder can separate from and/or crack the

glass substrate during a substantial change in climatic temperature. This situation is known as thermal shock.

U.S. Patent number 6,319,461, issued to Domi *et al.* discloses a lead free solder for soldering to a ceramic or glass substrate to resist thermal shock. The Domi *et al.* invention includes titanium as its essential component in combating thermal shock; however, the price and properties of titanium when included in a solder give rise to concerns over cost and workability of the solder at certain temperatures. As a result, the titanium laden Domi *et al.* solder composition is restricted to a liquids temperature not greater than 400°C.

10 A need exists in the art for a cost-effective, workable, lead-free solder composition suitable for use on a glass substrate having a low coefficient of thermal expansion to reduce the likelihood of thermal shock to a glass substrate.

SUMMARY

The present invention has been developed to overcome many limitations and disadvantages of known lead-free solders, and to generally fulfill a need in the art for a lead-free solder composition having a low coefficient of thermal expansion to reduce the likelihood of thermal shock to a glass substrate.

The present invention provides a lead-free solder composition for soldering to a glass substrate, wherein the solder composition includes tin (Sn) and silver (Ag) as well as a granular additive material having a low coefficient of thermal expansion to combat thermal shock and the percent weight of the solder and granular additive are at least 97% and at least 3%, respectively.

The solder composition of the present invention can further include bismuth (Bi) wherein the percent weight of the solder, including bismuth, is between 61% and 39% tin (Sn), between 1% - 3% silver (Ag) and between 59% and 37% bismuth (Bi).

The granular additive of the present invention can be fused silica (SiO₂) or Invar®, encapsulated in a lead-free, wettable, metal alloy such as copper (Cu), nickel

(Ni) or silver (Ag). The granular additive may also be $36\% \pm 1\%$ weight nickel (Ni) alloy or $64\% \pm 1\%$ weight iron (Fe) alloy.

It is an object of the present invention to provide a lead-free solder composition which is cost effective, easy to manufacture, and easy to apply to a substrate.

5 It is another object of the present invention to provide a lead-free solder composition whose percent weight between solder and granular additive can be adjusted to coincide with the coefficient of thermal expansion of the substrate to which the solder is to be secured.

It is still another object of the present invention to be capable of use in
10 connection with a layer of indium to promote greater adhesion to a substrate.

The present invention also includes a solder composition including a mixture of elements having tin (Sn) and silver (Ag). A granular additive is also included which can be at least about 3% of the solder composition by weight. The granular additive can be a nickel iron alloy which includes about 36% nickel (Ni) and about 64% iron (Fe) by
15 weight.

In particular embodiments, the granular additive can be pretreated with flux. The flux can include zinc chloride, ammonium chloride and hydrochloric acid. The mixture of elements can include by weight about 95% - 97% tin (Sn) and about 5% - 3% silver (Ag). The mixture of elements can further include bismuth, in which the
20 mixture of elements can include by weight about 61% - 39% tin (Sn), about 59% - 37% bismuth (Bi) and about 1% - 3% silver (Ag).

In some embodiments, the granular additive can be about 30% of the solder composition by weight. In one such solder composition, the mixture of elements can include by weight about 95% tin (Sn) and about 5% silver (Ag). In another such solder
25 composition, the mixture of elements can include by weight about 75% tin (Sn), about 23% bismuth (Bi) and about 2% silver (Ag).

In other embodiments, the granular additive can be about 20% of the solder composition by weight. In one such embodiment, the mixture of elements can include by weight about 62% tin (Sn), about 36% bismuth (Bi) and about 2% silver (Ag). In

another such embodiment, the mixture of elements can include by weight about 72% tin (Sn), about 26% bismuth (Bi) and about 2% silver (Ag). In yet another such embodiment, the mixture of elements can include by weight about 78% tin (Sn), about 20% bismuth (Bi) and about 2% silver (Ag). In still another such embodiment, the mixture of elements can include by weight about 83% tin (Sn), about 15% bismuth (Bi) and about 2% silver (Ag). In a further such embodiment, the mixture of elements can include by weight about 88% tin (Sn), about 10% bismuth (Bi) and about 2% silver (Ag).

The present invention also includes a solder composition including a mixture of elements including tin and silver. A granular additive is also included and includes a material having a low coefficient of thermal expansion and can be at least about 3% of the solder composition by weight.

In particular embodiments, the granular additive can include iron, and can also include iron and nickel. In addition, the granular additive can be pretreated with flux which can include zinc chloride, ammonium chloride and hydrochloric acid.

The present invention also includes a method of forming a solder composition. A molten mixture of elements having tin and silver is formed. A granular additive is added to the molten mixture of elements. The granular additive can be at least about 3% of the solder composition by weight. The granular additive can be a nickel iron alloy which includes about 36% nickel (Ni) and about 64% iron (Fe) by weight.

In particular embodiments, the granular additive can be pretreated with flux before adding the granular additive to the molten mixture of elements.

The present invention also includes a method of forming a solder composition including forming a molten mixture of elements having tin and silver. A granular additive is added to the molten mixture of elements. The granular additive includes a material with a low coefficient of thermal expansion and can be at least about 3% of the solder composition by weight.

BRIEF DESCRIPTION OF THE DRAWINGS

The foregoing and other objects, features and advantages of the invention will be apparent from the following more particular description of particular embodiments of the invention, as illustrated in the accompanying drawings in which like reference
5 characters refer to the same parts throughout the different views. The drawings are not necessarily to scale, emphasis instead being placed upon illustrating the principles of the invention.

FIG. 1 is an assembly of a solder composition on a hardware component in accordance with an embodiment of the invention before melt.

10 FIG. 2 is an assembly of the solder composition secured to a hardware component and a substrate in accordance with an embodiment of the invention and including an enhanced bonding sub layer of Indium after melt.

DETAILED DESCRIPTION

Referring to FIGs. 1 and 2, an embodiment of a solder composition is shown
15 generally at 10 on a hardware component 20, such as a copper terminal, and a substrate 30. The solder composition 10 includes solder 12 and a granular additive 14 having a low coefficient of thermal expansion. The solder 12 includes tin and silver with a percent composition by weight of 95-97% tin (Sn) and between 5-3% silver (Ag).
Additionally, the solder 12 may also include bismuth (Bi), wherein said percent
20 composition by weight of the three components is 61-39% tin (Sn), 1-3% silver (Ag) and 59-37% bismuth (Bi).

As an alternative embodiment, for securing the solder to a glass substrate, the glass substrate may be coated with a layer of indium 46, approximately 50 microns thick, to improve bonding the hardware 20 to the substrate 30.

25 Further referring to FIGs. 1-2, the granular additive 14 with a low coefficient of thermal expansion is added to the solder 12. The granular additive 14 may be any wettable material having a low coefficient of thermal expansion such as fused silica, zirconium oxide, Invar®, or an alloy of 36% weight nickel (Ni) or 64% weight iron (Fe).

To improve wettability of the fused silica, it may be encapsulated in a metal such as copper, nickel, or silver. The size of the granular material 14 may range from 5 to 400 microns; however, particles ranging from 10 to 250 microns are preferred.

The percent weight of the solder 12 and granular material 14 for the solder composition 10 can be contingent upon the coefficient of thermal expansion of the substrate 30. By way of example, when using fused silica as the granular material 14, the percent weight of the solder composition 10 is at least 97% solder 12 and at least 3% granular material 14 to secure the solder composition 10 (and included hardware 20) to a glass substrate 30 having a coefficient of thermal expansion of 85×10^{-7} .

Referring specifically to FIG. 2, the solder composition 10 is placed on the hardware 20 and secured to the substrate 30 by conventional means, i.e., applying heat to melt the solder 12 and attach the hardware 20 to the substrate 30, thereby trapping the granular material 14 between the hardware 20 and the substrate 30. When the joined hardware 20 and substrate 30 are exposed to low climatic temperatures, the solder 12 can attempt to contract at a rate higher than that of the substrate 30; however, the trapped granular material 14 will prevent the high contraction rate of the solder 12 and adsorb the stress created by same, causing the substrate 30 to receive little or no stress from the contraction, thereby preventing thermal shock. If a layer of indium 46 (FIG. 1) is employed, a region 46a having a mixture of solder 12 and indium can be formed when melted.

In one embodiment, when preparing a solder composition 10 including granular Invar® as the granular additive 14, the mixture of elements of solder 12 can be first brought into a molten state. Flux is added to the granular Invar® and then the Invar® is mixed into the solder 12 to form the solder composition 10. The Invar®/flux mixture can be added to the solder 12 while wet or can be predried to reduce splattering. The flux pre-treats the Invar® and allows the Invar® to easily wet with the solder 12. The flux can be in liquid form and can contain for example, zinc chloride, ammonium chloride, and hydrochloric acid. When flux is used, encapsulation of the Invar®

granules by another metal is not necessary. Once mixed, the solder composition 10 can then be formed or cast into desired shapes.

The Invar® granules are typically spheres of an alloy that has about 36% nickel (Ni) by weight and about 64% iron (Fe) by weight. In one embodiment, the Invar® can have a particle size ranging from 50-140 microns. If desired, the Invar® with such a size can be sifted to remove particles below 100 microns so that particles having a size between about 100-140 microns can be added to the solder 12. The Invar® can in some embodiments be 20% - 30% of the solder composition 10 by weight, with the mixture of the elements of the solder 12 being the remaining 70% - 80% of the solder composition 10 by weight.

In addition to the composition ranges previously described for the solder composition 10, the Applicants have found particular solder compositions 10 that are suitable for soldering to glass. For example, in one solder composition 10, the solder 12 can be about 95% tin (Sn) and about 5% silver (Ag) by weight. In this solder composition 10, the 95Sn 5Ag solder 12 makes up about 70% of the weight of the solder composition 10 and the added Invar® makes up about 30%.

In another solder composition 10, the solder 12 can be about 75% tin (Sn), about 23% bismuth (Bi) and about 2% silver (Ag) by weight. In this solder composition 10, the 75Sn 23Bi 2Ag solder 12 makes up about 70% of the weight of the resulting solder composition 10 and the Invar® makes up about 30%.

In yet another solder composition 10, the solder 12 can be about 62% tin (Sn), about 36% bismuth (Bi) and about 2% silver (Ag) by weight. In this solder composition 10, the 62Sn 36Bi 2Ag solder 12 makes up about 80% of the weight of the solder composition 10 and the added Invar® makes up about 20%.

In still another solder composition 10, the solder 12 can be about 72% tin (Sn), about 26% bismuth (Bi) and about 2% silver (Ag) by weight. In this solder composition 10, the 72Sn 26Bi 2Ag solder 12 makes up about 80% of the weight of the solder composition 10 and the Invar® makes up about 20%.

In a further solder composition 10, the solder 12 can be about 78% tin (Sn), about 20% bismuth (Bi) and about 2% silver (Ag) by weight. In this solder composition 10, the 78Sn 20Bi 2Ag solder 12 makes up about 80% of the weight of the solder composition 10 and the Invar® makes up about 20%.

5 In yet a further solder composition 10, the solder 12 can be about 83% tin (Sn), about 15% bismuth (Bi) and about 2% silver (Ag) by weight. In this solder composition 10, the 83Sn 15Bi 2Ag solder 12 makes up about 80% of the weight of the solder composition 10 and the Invar® makes up about 20%.

10 In still a further solder composition 10, the solder 12 can be about 88% tin (Sn), about 10% bismuth (Bi) and about 2% silver (Ag) by weight. In this solder composition 10, the 88Sn 10Bi 2Ag solder 12 makes up about 80% of the weight of the solder composition 10 and the Invar® makes up about 20%.

While this invention has been particularly shown and described with references to particular embodiments thereof, it will be understood by those skilled in the art that
15 various changes in form and details may be made therein without departing from the scope of the invention encompassed by the appended claims. For example, although the solder composition 10 is suitable for use on glass, solder composition 10 can be used on other substrates and in other fields. In addition, although the solder composition 10 has been described as being melted by applying heat, in some embodiments, the solder
20 composition 10 can be used for spin soldering where friction generated by a spinning electrical terminal against a substrate heats and melts the solder composition 10 therebetween.

CLAIMS

What is claimed is:

1. A solder composition comprising:
a mixture of elements comprising tin (Sn) and silver (Ag); and
5 a granular additive which is at least about 3% of the solder composition by weight, the granular additive comprising a nickel iron alloy comprising about 36% nickel (Ni) and about 64% iron (Fe) , by weight.
2. The solder composition of Claim 1 in which the granular additive is pretreated with flux.
- 10 3. The solder composition of Claim 2 in which the flux comprises zinc chloride, ammonium chloride and hydrochloric acid.
4. The solder composition of Claim 1 in which the mixture of elements comprises by weight about 95% - 97% tin (Sn) and about 5% - 3% silver (Ag).
5. The solder composition of Claim 1 in which the mixture of elements further
15 comprises bismuth (Bi).
6. The solder composition of Claim 5 in which the mixture of elements comprises by weight about 61% - 39% tin (Sb), about 59% - 37% bismuth (Bi), and about 1% - 3% silver (Ag).
7. The solder composition of Claim 1 in which the granular additive is about 30%
20 of the solder composition by weight.

8. The solder composition of Claim 7, in which the mixture of elements comprises by weight about 95% tin (Sn), and about 5% silver (Ag).
9. The solder composition of Claim 7 in which the mixture of elements comprises by weight about 75% tin (Sn), about 23% bismuth (Bi) and about 2% silver (Ag).
5
10. The solder composition of Claim 1 in which the granular additive is about 20% of the solder composition by weight.
11. The solder composition of Claim 10 in which the mixture of elements comprises by weight about 62% tin (Sn), about 36% bismuth (Bi) and about 2% silver (Ag).
10
12. The solder composition of Claim 10 in which the mixture of elements comprises by weight about 72% tin (Sn), about 26% bismuth (Bi) and about 2% silver (Ag).
13. The solder composition of Claim 10 in which the mixture of elements comprises by weight about 78% tin (Sn), about 20% bismuth (Bi) and about 2% silver (Ag).
15
14. The solder composition of Claim 10 in which the mixture of elements comprises by weight about 83% tin (Sn), about 15% bismuth (Bi) and about 2% silver (Ag).
- 20 15. The solder composition of Claim 10 in which the mixture of elements comprises by weight about 88% tin (Sn), about 10% bismuth (Bi) and about 2% silver (Ag).

16. A solder composition comprising:
a mixture of elements comprising tin and silver; and
a granular additive comprising a material having a low coefficient of thermal expansion and being at least about 3% of the solder composition by weight.
17. The solder composition of Claim 16 in which the granular additive comprises iron.
18. The solder composition of Claim 16 in which the granular additive comprises iron and nickel.
19. The solder composition of Claim 16 in which the granular additive is pretreated with flux.
20. The solder composition of Claim 19 in which the flux comprises zinc chloride, ammonium chloride and hydrochloric acid.
21. A method of forming a solder composition comprising:
forming a molten mixture of elements comprising tin and silver; and
adding a granular additive to the molten mixture of elements, the granular additive being at least about 3% of the solder composition by weight, the granular additive comprising a nickel iron alloy comprising about 36% nickel (Ni) and about 64% iron (Fe), by weight.
22. The method of Claim 21 further comprising pretreating the granular additive with flux before adding the granular additive to the molten mixture of elements.

23. The method of Claim 22 further comprising pretreating the granular additive with flux comprising zinc chloride, ammonium chloride and hydrochloric acid.
24. The method of Claim 21 further comprising forming the molten mixture of elements to comprise by weight about 95% - 97% tin (Sn) and about 5% - 3% silver (Ag).
25. The method of Claim 21 further comprising including bismuth in the molten mixture of elements.
26. The method of Claim 25 further comprising forming the molten mixture of elements to comprise by weight about 61% - 39% tin (Sn), about 59% - 37% bismuth (Bi), and about 1% - 3% silver (Ag).
27. The method of Claim 21 further comprising adding an amount of the granular additive to comprise about 30% of the solder composition by weight.
28. The method of Claim 27 further comprising forming the molten mixture of elements to comprise by weight about 95% tin (Sn) and about 5% silver (Ag).
29. The method of Claim 27 further comprising forming the molten mixture of elements to comprise by weight about 75% tin (Sn), about 23% bismuth and about 2% silver.
30. The method of Claim 21 further comprising adding an amount of the granular additive to comprise about 20% of the solder composition by weight.

31. The method of Claim 30 further comprising forming the molten mixture of elements to comprise by weight about 62% tin (Sn), about 36% bismuth (Bi) and about 2% silver (Ag).
- 5 32. The method of Claim 30 further comprising forming the molten mixture of elements to comprise by weight about 72% tin (Sn), about 26% bismuth (Bi) and about 2% silver (Ag).
33. The method of Claim 30 further comprising forming the molten mixture of elements to comprise by weight about 78% tin (Sn), about 20% bismuth (Bi) and about 2% silver (Ag).
- 10 34. The method of Claim 30 further comprising forming the molten mixture of elements to comprise by weight about 83% tin (Sn), about 15% bismuth (Bi) and about 2% silver (Ag).
35. The method of Claim 30 further comprising forming the molten mixture of elements to comprise by weight about 88% tin (Sn), about 10% bismuth (Bi) and
15 about 2% silver (Ag).
36. A method of forming a solder composition comprising:
forming a molten mixture of elements comprising tin and silver; and
adding a granular additive to the molten mixture of elements, the
granular additive comprising a material with a low coefficient of thermal
20 expansion and being at least about 3% of the solder composition by weight.
37. The method of Claim 36 further comprising adding a granular additive comprising iron.

38. The method of Claim 36 further comprising adding a granular additive comprising iron and nickel.
39. The method of Claim 36 further comprising pretreating the granular additive with flux before adding the granular additive to the melting mixture of elements.
- 5 40. The method of Claim 39 further comprising pretreating the granular additive with flux comprising zinc chloride, ammonium chloride and hydrochloric acid.

ABSTRACT OF THE DISCLOSURE

The present invention relates to a lead-free solder composition having a low coefficient of thermal expansion to reduce the likelihood of thermal shock to a glass substrate. The solder composition includes a granular material added to lead-free solder
5 where the granular material may include fused silica, zirconium oxide, Invar®, or any wettable, lead-free alloy such as 36% weight nickel or 64% weight iron and the solder may include tin, silver and bismuth. When a component is soldered to a glass substrate by the present invention and exposed to a substantial change in climatic temperature the granular material counteracts and adsorbs the stress caused by contraction of the solder,
10 thereby preventing thermal shock to the glass substrate.

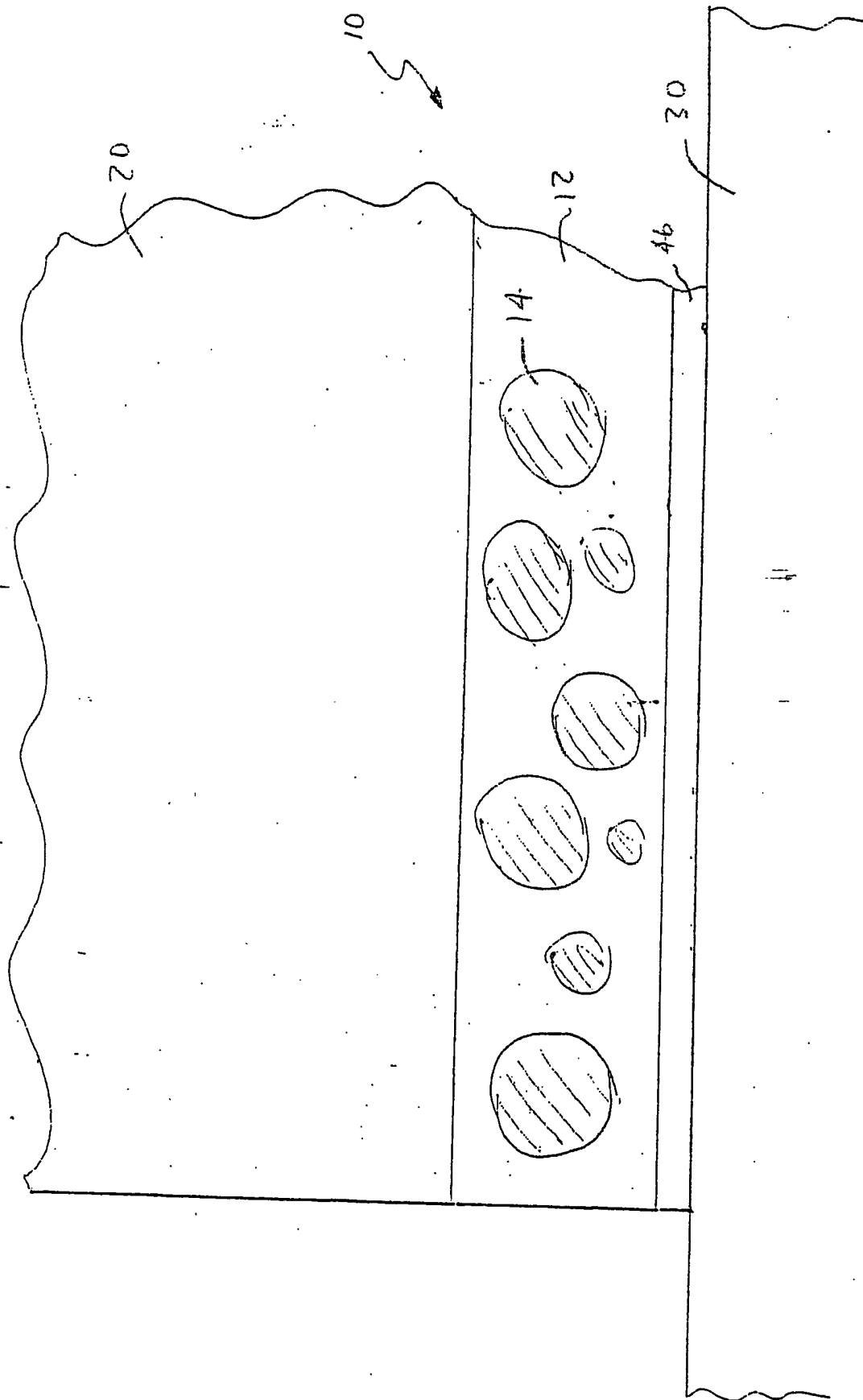


Fig. 1

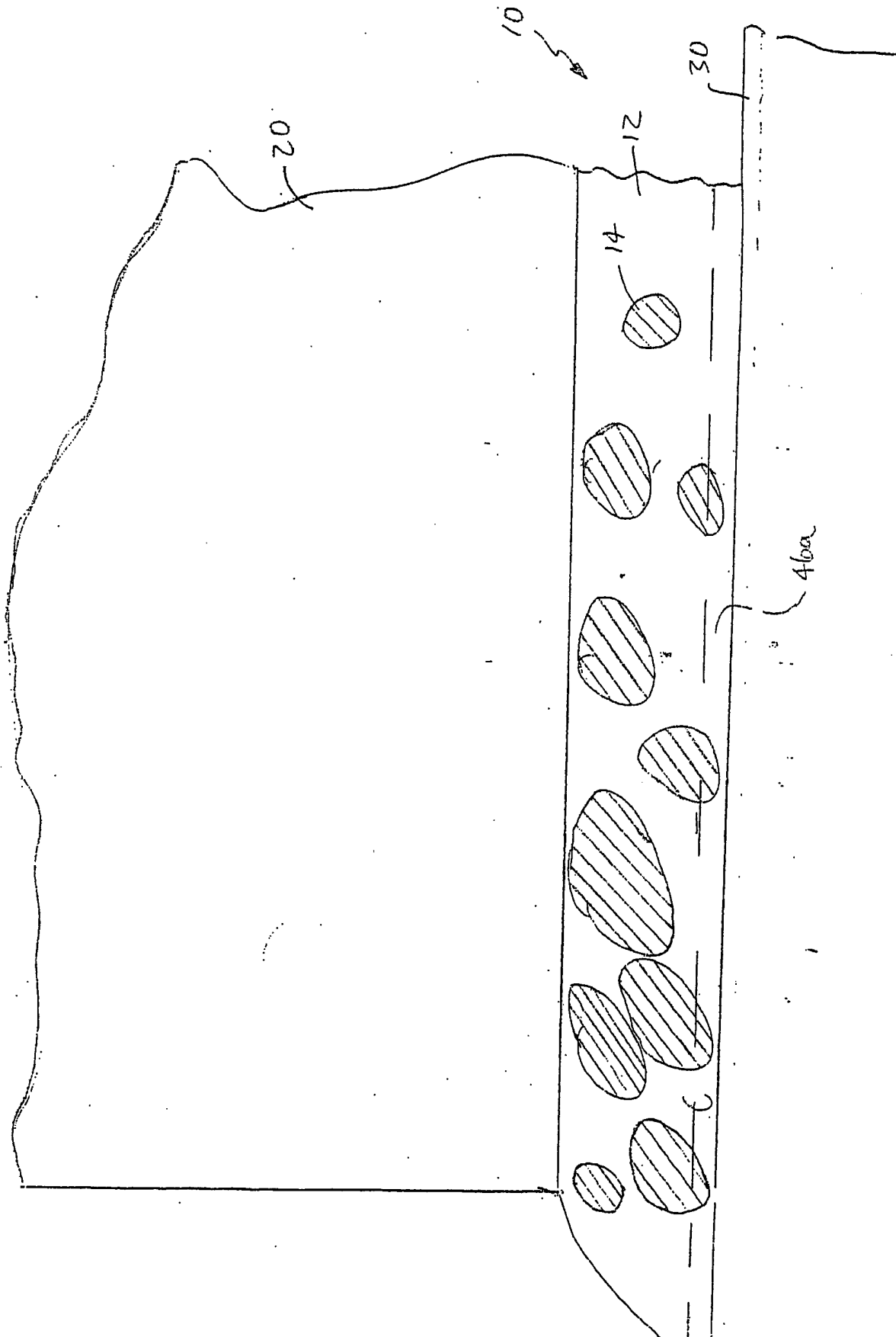


FIG. 2

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Declaration for Patent Application

[] Supplemental (37 C.F.R. §1.67)

As a named inventor, I hereby declare that:

My residence, mailing address and citizenship are as stated next to my name;

I believe I am the original, first and sole inventor (if only one name is listed) or an original, first and joint inventor (if plural names are listed in the signatory page(s) commencing at page 2 hereof) of the subject matter which is claimed and for which a patent is sought on the invention entitled

SOLDER COMPOSITION

the specification of which (check one)

- [] is attached hereto.
- [X] was filed on March 17, 2004 as United States Application Number 10/802,387.
- [] was filed on [PCT Filing Date] as PCT International Application No. [PCT Appl'n No.] [and assigned United States Application No. []].
- [] and was amended on [] (if applicable).

I hereby state that I have reviewed and understand the contents of the above-identified specification, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose information which is material to patentability as defined in 37 C.F.R. §1.56, including for continuation-in-part applications, material information which became available between the filing date of the prior application and the national or PCT international filing date of the continuation-in-part application.

I hereby claim foreign priority benefits under 35 U.S.C. 119 or 365 of any foreign application(s) for patent or inventor's certificate, or of any PCT international application which designated at least one country other than the United States of America, listed below and have also identified below, by checking the box, any foreign application for patent or inventor's certificate, or of any PCT international application having a filing date before that of the application on which priority is claimed:

<u>Prior Foreign Application(s)</u>			Priority Not Claimed	Certified Copy Filed?	
				YES	NO
_____ (Number)	_____ (Country)	_____ (Day/Month/Year filed)	[]	[]	[]
_____ (Number)	_____ (Country)	_____ (Day/Month/Year filed)	[]	[]	[]
_____ (Number)	_____ (Country)	_____ (Day/Month/Year filed)	[]	[]	[]

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

Full name of sole

or first inventor Premakaran T. Boaz

Inventor's Signature Date

Residence 16842 Yorkshire Street, Livonia, Michigan, 48154

Citizenship USA

Mailing Address same

Full name of second joint

inventor, if any John Pereira

Inventor's Signature Date

Residence 223 Agricultural Avenue, Rehoboth, Massachusetts, 02769

Citizenship USA

Mailing Address same

Full name of third joint

inventor, if any

Inventor's Signature Date

Residence

Citizenship

Mailing Address

Full name of fourth joint

inventor, if any

Inventor's Signature Date

Residence

Citizenship

Mailing Address

Joint

ASSIGNMENT

WHEREAS, we, **Premakaran T. Boaz and John Pereira**, have invented a certain improvement in **Solder Composition** described in an application for Patent,

- ☐ the specification of which is being executed on even date herewith and is about to be filed in the United States Patent Office (*use for utility (37 CFR § 1.53(b)) and design filings only*);
- ☐ is about to be filed in the United States Patent Office as a Provisional Application;
- ☒ the specification of which is United States Application No. **10/802,387**, filed **March 17, 2004**;
- ☐ the specification of which is a Patent Cooperation Treaty Application, International Application No. ☐, which designates the United States of America;
- ☐ which was patented under United States Patent No. ☐.

WHEREAS, **Antaya Technologies Corporation** (hereinafter "ASSIGNEE"), a corporation organized and existing under the laws of the **State of Rhode Island**, and having a usual place of business at **72 Fenner Street, Cranston, Rhode Island, 02910**, desires to acquire an interest therein in accordance with agreements duly entered into with us;

NOW, THEREFORE, to all whom it may concern be it known that for and in consideration of said agreements and of other good and valuable consideration, the receipt of which is hereby acknowledged, we have sold, assigned and transferred and by these presents do hereby sell, assign and transfer unto said ASSIGNEE, its successors, assigns and legal representatives, the entire right, title and interest in and throughout the United States of America, its territories and all foreign countries, in and to said invention as described in said application, together with the entire right, title and interest in and to said application and such Letters Patent as may issue on said invention; said invention, application and Letters Patent to be held and enjoyed by said ASSIGNEE for its own use and behalf and for its successors, assigns and legal representatives, to the full end of the term for which said Letters Patent may be granted as fully and entirely as the same would have been held by us had this assignment and sale not been made; we hereby convey all rights arising under or pursuant to any and all international agreements, treaties or laws relating to the protection of industrial property by filing any such applications for Letters Patent. We hereby acknowledge that this assignment, being of the entire right, title and interest in and to said invention, carries with it the right in ASSIGNEE to apply for and obtain from competent authorities in all countries of the world any and all Letters Patent by attorneys and agents of ASSIGNEE's selection and the right to procure the grant of all such Letters Patent to ASSIGNEE for its own name as assignee of the entire right, title and interest therein;

AND, we hereby further agree for ourselves and our executors and administrators to execute upon request any other lawful documents and likewise to perform any other lawful acts which may be deemed necessary to secure fully the aforesaid invention to said ASSIGNEE, its

successors, assigns and legal representatives, but at its or their expense and charges, including the execution of applications for patents in foreign countries, and the execution of any future applications including substitution, reissue, divisional or continuation applications, and preliminary or other statements and the giving of testimony in any interference or other proceeding in which said invention or any application or patent directed thereto may be involved;

AND, we do hereby authorize and request each Patent Office and the Commissioner of Patents of the United States to issue such Letters Patent as shall be granted upon said invention to said ASSIGNEE, its successors, assigns, and legal representatives.

IN TESTIMONY WHEREOF, we have hereunto set our hands and affixed our seals the date set forth below.

Inventor's Signature: _____

Premakaran T. Boaz

State/Commonwealth _____

of _____

County of _____

Then personally appeared before me the above-named **Premakaran T. Boaz** and acknowledged that he/she executed the foregoing instrument as his/her free act and deed this _____ day of _____, 20____.

(SEAL)

Notary Public

(print name)

My Commission expires ____/____/____

Inventor's Signature: _____

John Pereira

State/Commonwealth _____

of _____

County of _____

Then personally appeared before me the above-named **John Pereira** and acknowledged that he/she executed the foregoing instrument as his/her free act and deed this _____ day of _____, 20____.

(SEAL)

Notary Public

(print name)

My Commission expires ____/____/____

-1-

Date: 03/17/04 Express Mail Label No. **EV214952948US**

Inventors: Premakaran T. Boaz and John Pereira

Attorney's Docket No.: 2678.2011-000

SOLDER COMPOSITION

BACKGROUND

Generally speaking, solder is a material used to provide connections either between various items or to secure an item to a substrate. Solder is used in several
5 technical fields, such as electrical, mechanical, or thermal; however, the specific composition of solder or type of solder alloy varies widely between technical fields and even within a given field, depending on the application. Traditionally, solder largely consisted of lead as a result of its physical and chemical characteristics (i.e., wettability, melting point, rate of thermal expansion, etc.); however, lead solder became known as a
10 source of environmental pollution and federal legislation mandated a reduction in the content of lead in solder.

As a result, lead-free solder was introduced into various technical fields and is currently used for numerous applications without issue. As disclosed in U.S. patent numbers 5,066,544; 5,918,795; and 6,371,361, lead-free solder or reduced lead content
15 solder is successfully applied to soldering electronic components in both the microelectronic and conventional electronic fields.

However, there exist other technical fields where the aforementioned lead free solders are deficient. Within the technical field of soldering onto a substrate, such as an automobile window or windshield, known lead-free solders are less desirable because
20 they contain alloy compositions which possess a coefficient of thermal expansion nearly twice that of a glass substrate. As a result, the solder can separate from and/or crack the

glass substrate during a substantial change in climatic temperature. This situation is known as thermal shock.

U.S. Patent number 6,319,461, issued to Domi *et al.* discloses a lead free solder for soldering to a ceramic or glass substrate to resist thermal shock. The Domi *et al.*

5 invention includes titanium as its essential component in combating thermal shock; however, the price and properties of titanium when included in a solder give rise to concerns over cost and workability of the solder at certain temperatures. As a result, the titanium laden Domi *et al.* solder composition is restricted to a liquids temperature not greater than 400°C.

10 A need exists in the art for a cost-effective, workable, lead-free solder composition suitable for use on a glass substrate having a low coefficient of thermal expansion to reduce the likelihood of thermal shock to a glass substrate.

SUMMARY

The present invention has been developed to overcome many limitations and
15 disadvantages of known lead-free solders, and to generally fulfill a need in the art for a lead-free solder composition having a low coefficient of thermal expansion to reduce the likelihood of thermal shock to a glass substrate.

The present invention provides a lead-free solder composition for soldering to a glass substrate, wherein the solder composition includes tin (Sn) and silver (Ag) as well
20 as a granular additive material having a low coefficient of thermal expansion to combat thermal shock and the percent weight of the solder and granular additive are at least 97% and at least 3%, respectively.

The solder composition of the present invention can further include bismuth (Bi) wherein the percent weight of the solder, including bismuth, is between 61% and 39%
25 tin (Sn), between 1% - 3% silver (Ag) and between 59% and 37% bismuth (Bi).

The granular additive of the present invention can be fused silica (SiO₂) or Invar[®], encapsulated in a lead-free, wettable, metal alloy such as copper (Cu), nickel

(Ni) or silver (Ag). The granular additive may also be $36\% \pm 1\%$ weight nickel (Ni) alloy or $64\% \pm 1\%$ weight iron (Fe) alloy.

It is an object of the present invention to provide a lead-free solder composition which is cost effective, easy to manufacture, and easy to apply to a substrate.

5 It is another object of the present invention to provide a lead-free solder composition whose percent weight between solder and granular additive can be adjusted to coincide with the coefficient of thermal expansion of the substrate to which the solder is to be secured.

It is still another object of the present invention to be capable of use in
10 connection with a layer of indium to promote greater adhesion to a substrate.

The present invention also includes a solder composition including a mixture of elements having tin (Sn) and silver (Ag). A granular additive is also included which can be at least about 3% of the solder composition by weight. The granular additive can be a nickel iron alloy which includes about 36% nickel (Ni) and about 64% iron (Fe) by
15 weight.

In particular embodiments, the granular additive can be pretreated with flux. The flux can include zinc chloride, ammonium chloride and hydrochloric acid. The mixture of elements can include by weight about 95% - 97% tin (Sn) and about 5% - 3% silver (Ag). The mixture of elements can further include bismuth, in which the
20 mixture of elements can include by weight about 61% - 39% tin (Sn), about 59% - 37% bismuth (Bi) and about 1% - 3% silver (Ag).

In some embodiments, the granular additive can be about 30% of the solder composition by weight. In one such solder composition, the mixture of elements can include by weight about 95% tin (Sn) and about 5% silver (Ag). In another such solder
25 composition, the mixture of elements can include by weight about 75% tin (Sn), about 23% bismuth (Bi) and about 2% silver (Ag).

In other embodiments, the granular additive can be about 20% of the solder composition by weight. In one such embodiment, the mixture of elements can include by weight about 62% tin (Sn), about 36% bismuth (Bi) and about 2% silver (Ag). In

another such embodiment, the mixture of elements can include by weight about 72% tin (Sn), about 26% bismuth (Bi) and about 2% silver (Ag). In yet another such embodiment, the mixture of elements can include by weight about 78% tin (Sn), about 20% bismuth (Bi) and about 2% silver (Ag). In still another such embodiment, the mixture of elements can include by weight about 83% tin (Sn), about 15% bismuth (Bi) and about 2% silver (Ag). In a further such embodiment, the mixture of elements can include by weight about 88% tin (Sn), about 10% bismuth (Bi) and about 2% silver (Ag).

The present invention also includes a solder composition including a mixture of elements including tin and silver. A granular additive is also included and includes a material having a low coefficient of thermal expansion and can be at least about 3% of the solder composition by weight.

In particular embodiments, the granular additive can include iron, and can also include iron and nickel. In addition, the granular additive can be pretreated with flux which can include zinc chloride, ammonium chloride and hydrochloric acid.

The present invention also includes a method of forming a solder composition. A molten mixture of elements having tin and silver is formed. A granular additive is added to the molten mixture of elements. The granular additive can be at least about 3% of the solder composition by weight. The granular additive can be a nickel iron alloy which includes about 36% nickel (Ni) and about 64% iron (Fe) by weight.

In particular embodiments, the granular additive can be pretreated with flux before adding the granular additive to the molten mixture of elements.

The present invention also includes a method of forming a solder composition including forming a molten mixture of elements having tin and silver. A granular additive is added to the molten mixture of elements. The granular additive includes a material with a low coefficient of thermal expansion and can be at least about 3% of the solder composition by weight.

BRIEF DESCRIPTION OF THE DRAWINGS

The foregoing and other objects, features and advantages of the invention will be apparent from the following more particular description of particular embodiments of the invention, as illustrated in the accompanying drawings in which like reference
5 characters refer to the same parts throughout the different views. The drawings are not necessarily to scale, emphasis instead being placed upon illustrating the principles of the invention.

FIG. 1 is an assembly of a solder composition on a hardware component in accordance with an embodiment of the invention before melt.

10 FIG. 2 is an assembly of the solder composition secured to a hardware component and a substrate in accordance with an embodiment of the invention and including an enhanced bonding sub layer of Indium after melt.

DETAILED DESCRIPTION

Referring to FIGs. 1 and 2, an embodiment of a solder composition is shown
15 generally at 10 on a hardware component 20, such as a copper terminal, and a substrate 30. The solder composition 10 includes solder 12 and a granular additive 14 having a low coefficient of thermal expansion. The solder 12 includes tin and silver with a percent composition by weight of 95-97% tin (Sn) and between 5-3% silver (Ag). Additionally, the solder 12 may also include bismuth (Bi), wherein said percent
20 composition by weight of the three components is 61-39% tin (Sn), 1-3% silver (Ag) and 59-37% bismuth (Bi).

As an alternative embodiment, for securing the solder to a glass substrate, the glass substrate may be coated with a layer of indium 46, approximately 50 microns thick, to improve bonding the hardware 20 to the substrate 30.

25 Further referring to FIGs. 1-2, the granular additive 14 with a low coefficient of thermal expansion is added to the solder 12. The granular additive 14 may be any wettable material having a low coefficient of thermal expansion such as fused silica, zirconium oxide, Invar®, or an alloy of 36% weight nickel (Ni) or 64% weight iron (Fe).

To improve wettability of the fused silica, it may be encapsulated in a metal such as copper, nickel, or silver. The size of the granular material 14 may range from 5 to 400 microns; however, particles ranging from 10 to 250 microns are preferred.

The percent weight of the solder 12 and granular material 14 for the solder composition 10 can be contingent upon the coefficient of thermal expansion of the substrate 30. By way of example, when using fused silica as the granular material 14, the percent weight of the solder composition 10 is at least 97% solder 12 and at least 3% granular material 14 to secure the solder composition 10 (and included hardware 20) to a glass substrate 30 having a coefficient of thermal expansion of 85×10^{-7} .

Referring specifically to FIG. 2, the solder composition 10 is placed on the hardware 20 and secured to the substrate 30 by conventional means, i.e., applying heat to melt the solder 12 and attach the hardware 20 to the substrate 30, thereby trapping the granular material 14 between the hardware 20 and the substrate 30. When the joined hardware 20 and substrate 30 are exposed to low climatic temperatures, the solder 12 can attempt to contract at a rate higher than that of the substrate 30; however, the trapped granular material 14 will prevent the high contraction rate of the solder 12 and adsorb the stress created by same, causing the substrate 30 to receive little or no stress from the contraction, thereby preventing thermal shock. If a layer of indium 46 (FIG. 1) is employed, a region 46a having a mixture of solder 12 and indium can be formed when melted.

In one embodiment, when preparing a solder composition 10 including granular Invar® as the granular additive 14, the mixture of elements of solder 12 can be first brought into a molten state. Flux is added to the granular Invar® and then the Invar® is mixed into the solder 12 to form the solder composition 10. The Invar®/flux mixture can be added to the solder 12 while wet or can be predried to reduce splattering. The flux pre-treats the Invar® and allows the Invar® to easily wet with the solder 12. The flux can be in liquid form and can contain for example, zinc chloride, ammonium chloride, and hydrochloric acid. When flux is used, encapsulation of the Invar®

granules by another metal is not necessary. Once mixed, the solder composition 10 can then be formed or cast into desired shapes.

The Invar® granules are typically spheres of an alloy that has about 36% nickel (Ni) by weight and about 64% iron (Fe) by weight. In one embodiment, the Invar® can have a particle size ranging from 50-140 microns. If desired, the Invar® with such a size can be sifted to remove particles below 100 microns so that particles having a size between about 100-140 microns can be added to the solder 12. The Invar® can in some embodiments be 20% - 30% of the solder composition 10 by weight, with the mixture of the elements of the solder 12 being the remaining 70% - 80% of the solder composition 10 by weight.

In addition to the composition ranges previously described for the solder composition 10, the Applicants have found particular solder compositions 10 that are suitable for soldering to glass. For example, in one solder composition 10, the solder 12 can be about 95% tin (Sn) and about 5% silver (Ag) by weight. In this solder composition 10, the 95Sn 5Ag solder 12 makes up about 70% of the weight of the solder composition 10 and the added Invar® makes up about 30%.

In another solder composition 10, the solder 12 can be about 75% tin (Sn), about 23% bismuth (Bi) and about 2% silver (Ag) by weight. In this solder composition 10, the 75Sn 23Bi 2Ag solder 12 makes up about 70% of the weight of the resulting solder composition 10 and the Invar® makes up about 30%.

In yet another solder composition 10, the solder 12 can be about 62% tin (Sn), about 36% bismuth (Bi) and about 2% silver (Ag) by weight. In this solder composition 10, the 62Sn 36Bi 2Ag solder 12 makes about 80% of the weight of the solder composition 10 and the added Invar® makes up about 20%.

In still another solder composition 10, the solder 12 can be about 72% tin (Sn), about 26% bismuth (Bi) and about 2% silver (Ag) by weight. In this solder composition 10, the 72Sn 26Bi 2Ag solder 12 makes up about 80% of the weight of the solder composition 10 and the Invar® makes up about 20%.

In a further solder composition 10, the solder 12 can be about 78% tin (Sn), about 20% bismuth (Bi) and about 2% silver (Ag) by weight. In this solder composition 10, the 78Sn 20Bi 2Ag solder 12 makes up about 80% of the weight of the solder composition 10 and the Invar® makes up about 20%.

5 In yet a further solder composition 10, the solder 12 can be about 83% tin (Sn), about 15% bismuth (Bi) and about 2% silver (Ag) by weight. In this solder composition 10, the 83Sn 15Bi 2Ag solder 12 makes up about 80% of the weight of the solder composition 10 and the Invar® makes up about 20%.

10 In still a further solder composition 10, the solder 12 can be about 88% tin (Sn), about 10% bismuth (Bi) and about 2% silver (Ag) by weight. In this solder composition 10, the 88Sn 10Bi 2Ag solder 12 makes up about 80% of the weight of the solder composition 10 and the Invar® makes up about 20%.

While this invention has been particularly shown and described with references to particular embodiments thereof, it will be understood by those skilled in the art that
15 various changes in form and details may be made therein without departing from the scope of the invention encompassed by the appended claims. For example, although the solder composition 10 is suitable for use on glass, solder composition 10 can be used on other substrates and in other fields. In addition, although the solder composition 10 has been described as being melted by applying heat, in some embodiments, the solder
20 composition 10 can be used for spin soldering where friction generated by a spinning electrical terminal against a substrate heats and melts the solder composition 10 therebetween.

CLAIMS

What is claimed is:

1. A solder composition comprising:
a mixture of elements comprising tin (Sn) and silver (Ag); and
5 a granular additive which is at least about 3% of the solder composition by weight, the granular additive comprising a nickel iron alloy comprising about 36% nickel (Ni) and about 64% iron (Fe) , by weight.
2. The solder composition of Claim 1 in which the granular additive is pretreated with flux.
- 10 3. The solder composition of Claim 2 in which the flux comprises zinc chloride, ammonium chloride and hydrochloric acid.
4. The solder composition of Claim 1 in which the mixture of elements comprises by weight about 95% - 97% tin (Sn) and about 5% - 3% silver (Ag).
5. The solder composition of Claim 1 in which the mixture of elements further
15 comprises bismuth (Bi).
6. The solder composition of Claim 5 in which the mixture of elements comprises by weight about 61% - 39% tin (Sb), about 59% - 37% bismuth (Bi), and about 1% - 3% silver (Ag).
7. The solder composition of Claim 1 in which the granular additive is about 30%
20 of the solder composition by weight.

8. The solder composition of Claim 7, in which the mixture of elements comprises by weight about 95% tin (Sn), and about 5% silver (Ag).
9. The solder composition of Claim 7 in which the mixture of elements comprises by weight about 75% tin (Sn), about 23% bismuth (Bi) and about 2% silver (Ag).
5
10. The solder composition of Claim 1 in which the granular additive is about 20% of the solder composition by weight.
11. The solder composition of Claim 10 in which the mixture of elements comprises by weight about 62% tin (Sn), about 36% bismuth (Bi) and about 2% silver (Ag).
10
12. The solder composition of Claim 10 in which the mixture of elements comprises by weight about 72% tin (Sn), about 26% bismuth (Bi) and about 2% silver (Ag).
13. The solder composition of Claim 10 in which the mixture of elements comprises by weight about 78% tin (Sn), about 20% bismuth (Bi) and about 2% silver (Ag).
15
14. The solder composition of Claim 10 in which the mixture of elements comprises by weight about 83% tin (Sn), about 15% bismuth (Bi) and about 2% silver (Ag).
- 20 15. The solder composition of Claim 10 in which the mixture of elements comprises by weight about 88% tin (Sn), about 10% bismuth (Bi) and about 2% silver (Ag).

16. A solder composition comprising:
a mixture of elements comprising tin and silver; and
a granular additive comprising a material having a low coefficient of
thermal expansion and being at least about 3% of the solder composition by
weight.
17. The solder composition of Claim 16 in which the granular additive comprises
iron.
18. The solder composition of Claim 16 in which the granular additive comprises
iron and nickel.
19. The solder composition of Claim 16 in which the granular additive is pretreated
with flux.
20. The solder composition of Claim 19 in which the flux comprises zinc chloride,
ammonium chloride and hydrochloric acid.
21. A method of forming a solder composition comprising:
forming a molten mixture of elements comprising tin and silver; and
adding a granular additive to the molten mixture of elements, the
granular additive being at least about 3% of the solder composition by weight,
the granular additive comprising a nickel iron alloy comprising about 36%
nickel (Ni) and about 64% iron (Fe), by weight.
22. The method of Claim 21 further comprising pretreating the granular additive
with flux before adding the granular additive to the molten mixture of elements.

23. The method of Claim 22 further comprising pretreating the granular additive with flux comprising zinc chloride, ammonium chloride and hydrochloric acid.
24. The method of Claim 21 further comprising forming the molten mixture of elements to comprise by weight about 95% - 97% tin (Sn) and about 5% - 3% silver (Ag).
25. The method of Claim 21 further comprising including bismuth in the molten mixture of elements.
26. The method of Claim 25 further comprising forming the molten mixture of elements to comprise by weight about 61% - 39% tin (Sn), about 59% - 37% bismuth (Bi), and about 1% - 3% silver (Ag).
27. The method of Claim 21 further comprising adding an amount of the granular additive to comprise about 30% of the solder composition by weight.
28. The method of Claim 27 further comprising forming the molten mixture of elements to comprise by weight about 95% tin (Sn) and about 5% silver (Ag).
29. The method of Claim 27 further comprising forming the molten mixture of elements to comprise by weight about 75% tin (Sn), about 23% bismuth and about 2% silver.
30. The method of Claim 21 further comprising adding an amount of the granular additive to comprise about 20% of the solder composition by weight.

31. The method of Claim 30 further comprising forming the molten mixture of elements to comprise by weight about 62% tin (Sn), about 36% bismuth (Bi) and about 2% silver (Ag).
- 5 32. The method of Claim 30 further comprising forming the molten mixture of elements to comprise by weight about 72% tin (Sn), about 26% bismuth (Bi) and about 2% silver (Ag).
33. The method of Claim 30 further comprising forming the molten mixture of elements to comprise by weight about 78% tin (Sn), about 20% bismuth (Bi) and about 2% silver (Ag).
- 10 34. The method of Claim 30 further comprising forming the molten mixture of elements to comprise by weight about 83% tin (Sn), about 15% bismuth (Bi) and about 2% silver (Ag).
35. The method of Claim 30 further comprising forming the molten mixture of elements to comprise by weight about 88% tin (Sn), about 10% bismuth (Bi) and
15 about 2% silver (Ag).
36. A method of forming a solder composition comprising:
forming a molten mixture of elements comprising tin and silver; and
adding a granular additive to the molten mixture of elements, the
granular additive comprising a material with a low coefficient of thermal
20 expansion and being at least about 3% of the solder composition by weight.
37. The method of Claim 36 further comprising adding a granular additive comprising iron.

38. The method of Claim 36 further comprising adding a granular additive comprising iron and nickel.
39. The method of Claim 36 further comprising pretreating the granular additive with flux before adding the granular additive to the melting mixture of elements.
- 5 40. The method of Claim 39 further comprising pretreating the granular additive with flux comprising zinc chloride, ammonium chloride and hydrochloric acid.

ABSTRACT OF THE DISCLOSURE

The present invention relates to a lead-free solder composition having a low coefficient of thermal expansion to reduce the likelihood of thermal shock to a glass substrate. The solder composition includes a granular material added to lead-free solder
5 where the granular material may include fused silica, zirconium oxide, Invar®, or any wettable, lead-free alloy such as 36% weight nickel or 64% weight iron and the solder may include tin, silver and bismuth. When a component is soldered to a glass substrate by the present invention and exposed to a substantial change in climatic temperature the granular material counteracts and adsorbs the stress caused by contraction of the solder,
10 thereby preventing thermal shock to the glass substrate.

Tit^l SOLDER COMPOSITION
Inventors: Premakaran T. Boaz, *et al.*

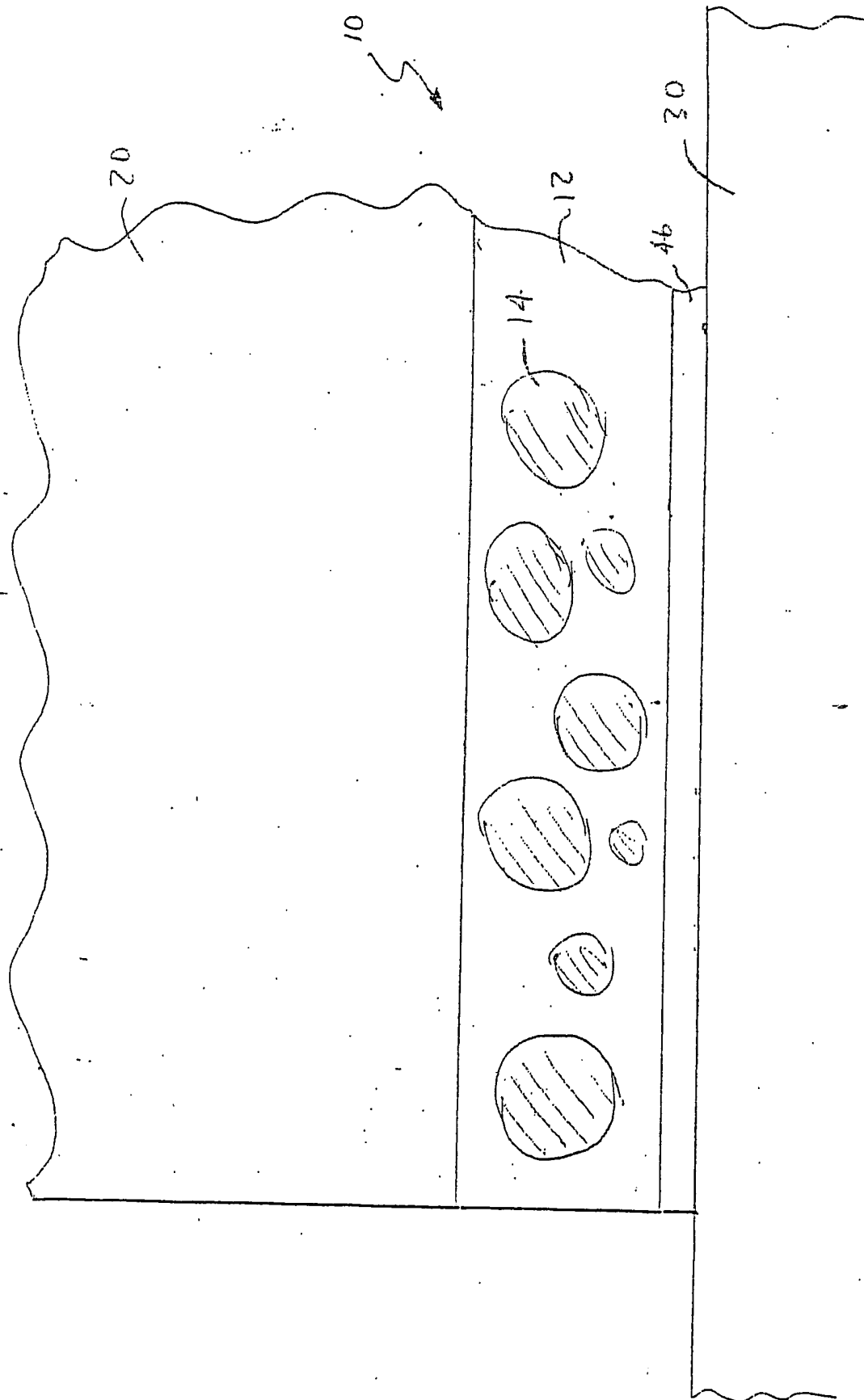


Fig. 1

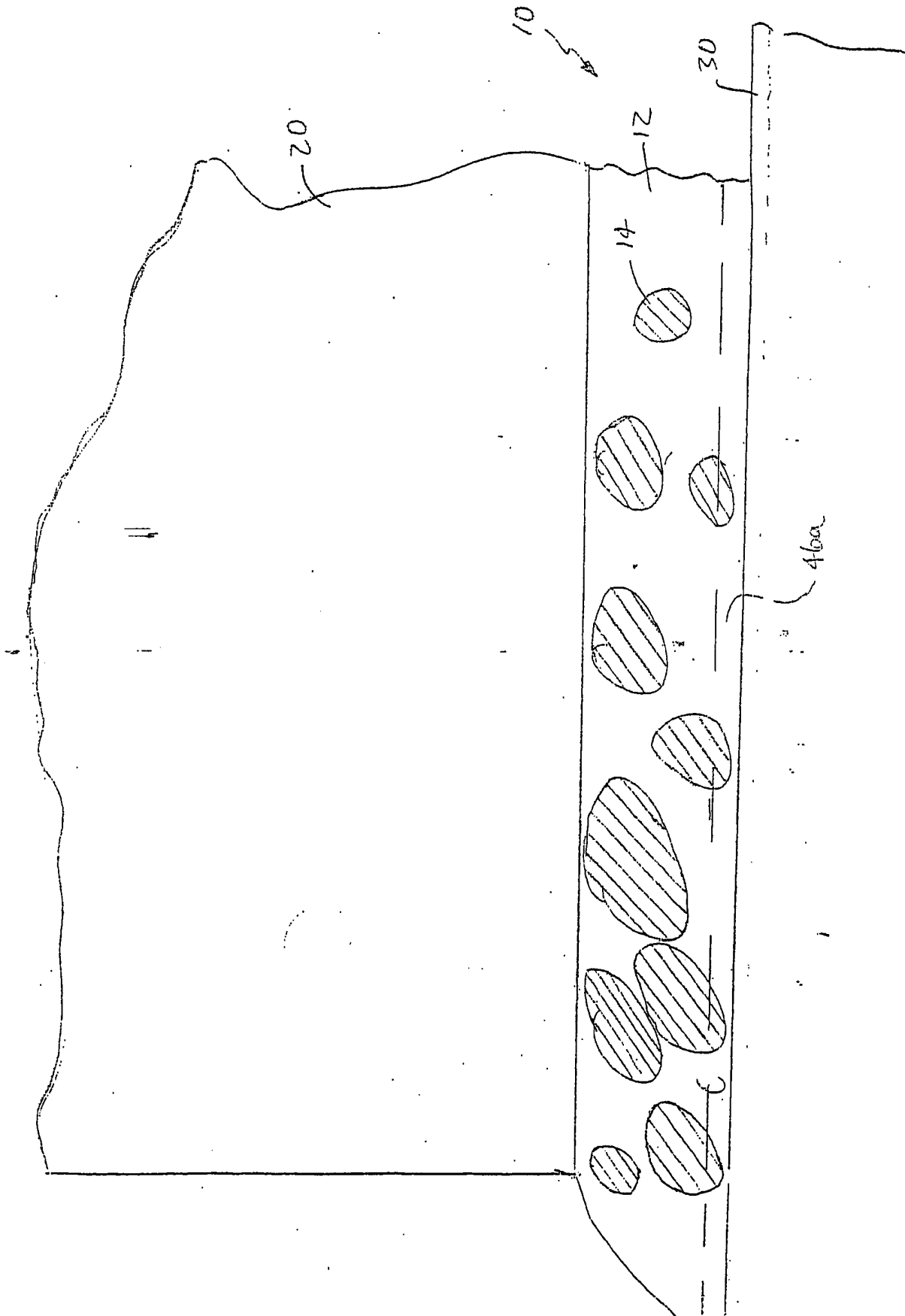


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